

Kinetic Controls on the Desorption/Dissolution of Sorbed U(VI) and Their Influence on Reactive Transport

John M. Zachara*, Chongxuan Liu, Nikolla P. Qafoku, James P. McKinley (PNNL); Jeffrey G. Catalano and Gordon E. Brown, Jr. (Stanford Univ.); and James A. Davis (USGS)

Office of Biological and Environmental Research
Environmental Remediation Sciences Program (ERSP)

*Pacific Northwest National Laboratory, Richland, WA 99354

BACKGROUND

A number of published studies have sought to understand geochemical kinetic process of uranium (U) that are relevant to nuclear waste sites and repositories by studying the weathering of U ore bodies and downgradient transport of weathering products. Such studies have provided important insights on processes operative over many thousands to millions of years. This project also seeks knowledge on the geochemical kinetics of U, but for shorter in-ground time periods (e.g., 20-50 years) relevant to DOE legacy waste sites. Several representative field sites were selected for intense study at Hanford as part of EMSP research to provide: i.) fundamental insights on intermediate duration geochemical events of U controlling fate and transport, and ii.) key scientific information needed for remedial action assessment and informed decision making.

The site discussed in this poster is the 300 A uranium plume. This plume is located at the south end of Hanford and discharges directly to the Columbia River (see right). The plume resulted from the discharge of fuel fabrication wastes (nitric acid solutions containing U and Cu) and cladding dissolution wastes (basic sodium aluminate) to the North and South Process Ponds between 1943 and 1975 near the Columbia River (see right). A Kd-based remedial action assessment fifteen years ago predicted that the plume would dissipate to concentrations below the DWS within 10 y. As a result of this assessment, an interim, MNA remedial decision was agreed to by DOE and state/federal regulators. It has been 15 y since the above assessment, and groundwater concentrations have not decreased (attenuated) as projected. Stakeholders are now demanding remedial intervention, and DOE seeks science-based conceptual and numeric models for more accurate future projections.

OBJECTIVES

- Identify the chemical speciation (e.g., adsorption complexes or precipitates), mineral residence, and physical location of contaminant U in a depth sequence of sediments from the disposal source to groundwater.
- Measure desorption/dissolution rates of sorbed U(VI), quantify controlling factors, and develop descriptive kinetic models to provide a scientific basis to forecast U(VI) fluxes to groundwater, future plume dynamics, and long-term contaminant attenuation.
- Establish reaction networks and determine geochemically/physically realistic reaction parameters to drive state-of-the-art reactive transport modeling of U in vadose zone pore fluids and groundwater.

METHODS

- Sediments collected from excavations in the historic process ponds (see right).
- Bulk x-ray absorption spectroscopy (EXAFS) and cryogenic laser-induced fluorescence spectroscopy (CLIFS) to determine U(VI) molecular environment.
- X-ray and electron microscope, and transmission and scanning electron microscopy for spatial distribution, element association, and physical location mapping.
- Batch experiments at different solid-to-solution ratios to evaluate rates and equilibrium states of adsorption and solubility reactions.
- Column experiments of different sizes to assess in-situ rates of desorption/dissolution, mass transfer effects, and reaction parameter scaling.

PUBLICATIONS

Bond, D. L., J. A. Davis, and J. M. Zachara. 2006. Uranium(VI) dissolution and desorption from contaminated vadose zone sediments. *Geochimica et Cosmochimica Acta* (Accepted).

Catalano, J. G., J. P. McKinley, J. M. Zachara, S. C. Smith, and G. E. Brown, Jr. 2006. Changes in uranium speciation through a depth sequence of contaminated Hanford sediments. *Environ. Sci. Technol.*, ASAP Article; DOI: [10.1021/es052096g](https://doi.org/10.1021/es052096g).

Qafoku, N. P., J. M. Zachara, C. Liu, P. L. Gassman, O. S. Qafoku, and S. C. Smith. 2005. Kinetic desorption and sorption of U(VI) during reactive transport in a contaminated Hanford sediment. *Environ. Sci. Technol.*, 39:3157-3165.

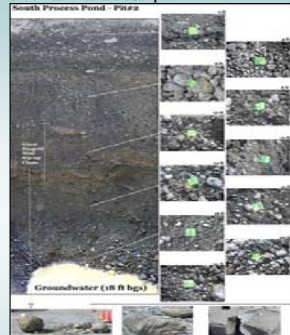
Wang, Z., J. M. Zachara, J. P. McKinley, S. C. Smith, and S. M. Heald. 2005. Cryogenic laser induced U(VI) fluorescence studies of a U(VI) substituted natural caliche: Implications to U(VI) speciation in contaminated Hanford sediments. *Environ. Sci. Technol.*, 39:2651-2659.

HANFORD 300 A URANIUM PLUME

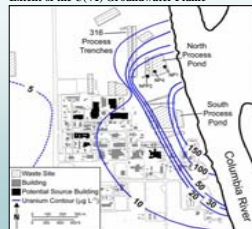
The North Process Pond



One of Four Excavations Sampled



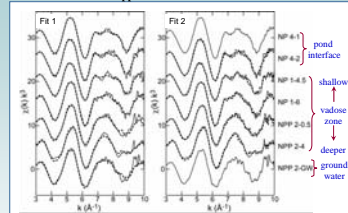
Extent of the U(VI) Groundwater Plume



- The vadose zone is physically complex in this location and contained U(VI) concentrations ranging from background (~3 mg/kg) to over 4000 mg/kg. Most vadose zone samples contained 15-150 mg/kg U(VI).
- The most contaminated sediments were excavated as part of source term mitigation. These were sampled and analyzed here (NP).
- Significant sorbed U(VI) was present on aquifer fines.

CONCEPTUAL MODEL OF CHEMICAL SPECIATION

Two Fit Models were Applied to the EXAFS Data



Results of Linear Combination Fitting

Fit	NP-4.1	NP-4.2	NP-1.4.5	NP-1.6	NP-2.6.5	NP-2.4	NP-2.6.7
Liebigite	0.42(4)	0.23(4)	0.45(4)	0.34(4)	0.00(5)	0.00(0)	0.00(0)
U(VI)-metformin/metallotheorite	0.42(4)	0.23(4)	0.37(6)	0.54(6)	0.84(8)	0.54(6)	0.87(9)
Metatbernite	0.00(0)	0.00(0)	0.00(4)	0.11(4)	0.05(5)	0.41(4)	0.08(6)
Component Sum	0.92	0.94	0.83	0.98	0.89	0.95	0.89
χ^2	0.05	0.16	0.17	0.18	0.28	0.18	0.42

Fit	NP-4.1	NP-4.2	NP-1.4.5	NP-1.6	NP-2.6.5	NP-2.4	NP-2.6.7
NP-4.1	1	1.00(5)	0.98(4)	0.75(4)	0.16(4)	0.02(4)	0
NP-2.6.7	0	0.03(6)	0.00(5)	0.17(5)	0.63(5)	0.43(5)	1
Metatbernite	0	0.00(0)	0.00(2)	0.15(2)	0.22(2)	0.55(2)	0
Component Sum	1	1.03	0.98	1.00	1.00	1	1
χ^2	N/A	0.23	0.15	0.16	0.16	0.15	N/A

*Estimated standard deviations of the final fits are shown in parentheses.
*Sum of fractional fit components.
*Chi-squared, a goodness-of-fit parameter.

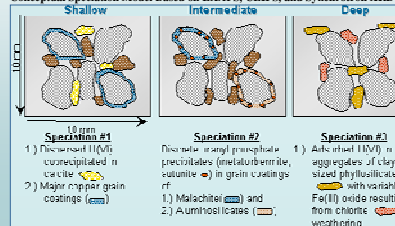
- EXAFS was performed on samples with U(VI)_{TR} > 75 mg/kg.
- Two linear combination fit approaches were tried to estimate species distribution
- Fit 1 – Based on model compound spectra: Liebigite ($\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$), metatbernite ($\text{Cu}(\text{UO}_2\text{PO}_4) \cdot 8\text{H}_2\text{O}$), and smectite
- Fit 2 – Based on the assumption of NP-4.1 [U(VI) substituted calcite] and NP-2.6.7 [chlorite surface complexes] as “natural” reference spectra, and metatbernite as the only autinite-type phase.

- Although the goodness of fit parameters χ^2 were equivalent, Fit 2 was considered more realistic because CLIFS measurements showed that U(VI)-calcite, and not liebigite was present.

- The fitting procedure described each sample spectra as linear, fractional contributions of reference spectra.

- NP-2.6.5, for example is projected to contain 16% U(VI)-calcite, 22% metatbernite, and 66% adsorption complexes.

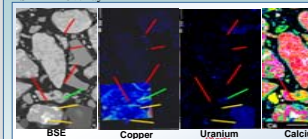
Conceptual Speciation Model Based on EXAFS, CLIFS, and Synchrotron XRD



- Three speciation regimes were tentatively identified.
- These were dominated by precipitates in the near-field and adsorption complexes down-gradient.
- Speciation differences resulted from waste-sediment reaction and U(VI) attenuation.

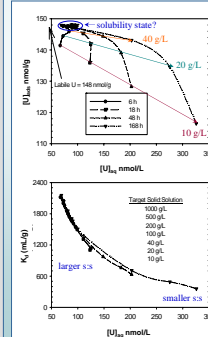
DISSOLUTION OF PRECIPITATED U(VI) FROM NPP2-4 [Speciation #2]

BSE-XRF Overlay



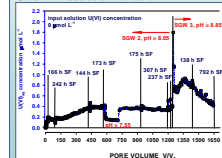
- Secondary Cu and Al/Si precipitates were observed as grain coatings. U(VI) was often found in these.
- Cu coatings include malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) and other unidentified phases.

Batch Dissolution with Varied Time ss



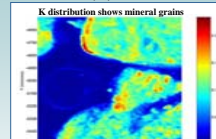
- Complex batch dissolution behavior.
- Strong kinetic behavior for smaller solid: solution ratios.
- Evidence for multiple phase contributions [U]_{ss}
- Solubility state is 75-95 nmol/L.

Column Dissolution Behavior

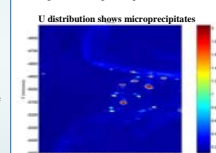


- Column dissolution shows strong pH/solubility effects, but minimal response to flow interruption.
- Effluents are under-saturated with $\text{Cu}(\text{UO}_2\text{PO}_4) \cdot 8\text{H}_2\text{O}$, but near saturation with CuO.
- Solubility state at pH ~8 (~400 nmol/L) is different from batch.

XRF of K and U(VI)



- Metatbernite/autinite precipitates are spatially heterogeneous and exist in grain coatings and porous solids.



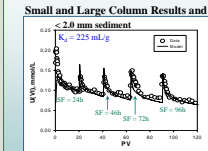
DESORPTION OF SURFACE COMPLEXED U(VI) FROM NPP1-14 [Speciation #3]

Unseived Sediment with River Cobble and Mud

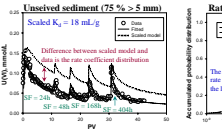


The sediment is river cobble with infilling of sand (10%), and silt and clay (~5%).

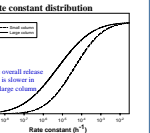
Small and Large Column Results and Rate Constant Distribution from the Distributed Rate Model (DRM)



Unseived sediment (75% > 5 mm)



Rate constant distribution



- A transport model containing K_d and a first order rate distribution was applied. K_d was found to scale in linear fashion with texture while the rate distribution did not. Mass transfer is very important for desorption.

IMPORTANT FINDINGS

- Sediment associated U(VI) resides in phyllosilicate and Cu grain coatings and in intra-grain domains of mm-sized lithic fragments that exist as fill between larger, rounded river gravel and cobble.
- The chemical speciation from precipitated U(VI) near the source (within calcite and as metatbernite) to adsorption complexes on Fe(III) oxide and aluminosilicates (chlorite primarily) in deeper vadose zone sediments and aquifer sediments.
- The desorption and dissolution behavior of sorbed U(VI) shows complex behavior, and its rate is slow. Both mass transfer and chemical kinetic effects appear to contribute. Precipitated U(VI) does not appear to dissolve to equilibrium. Phase transformations may be occurring.
- Equilibrium parameters for adsorption reactions measured on fine-textured isolates scale to the in-situ texture. Mass-transfer parameters, in contrast, do not. Future research will strive to understand factors controlling the kinetic reactions at different scales.